Formation of submicron-thick oxide barrier for reducing AC loss in multifilamentary Bi2223 tapes

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Formation of Submicron-Thick Oxide Barrier for Reducing AC Loss in Multifilamentary Bi2223 Tapes

K. Osamura, N. Wada, T. Ogawa, and F. Nakao

***Abstract*—Barrier surrounding oxide superconducting core is effective in reducing AC loss of the multifilamentary tape. Metallic magnesium was chosen as its precursor material. Through the ordinary deformation process to fabricate the tape, the magnesium layer was easily thinned up to sub-micron. By the successive oxidation treatment, the barrier became stable MgO layer. Usefulness of ductile material has been demonstrated to produce ultra-thin barrier.**

***Index Terms*—AC loss, barrier, BSCCO2223, Mg, oxidation.**

I. Introduction

IT IS inevitable to reduce AC loss of the present commercial BSCCO2223 tapes for practical application. Especially the multifilamentary tapes have large coupling current losses. One solution to reduce such coupling loss is to surround simply the superconducting filaments with high-resistive materials. Ceramics have been examined as barrier material by many investigators; BaZrO3 and SrZrO3 [1], SrCO3 [2], [3]. Many attempts however, resulted in the fact that the coupling current loss characteristics could be improved appreciably, but the transport critical current degraded and the fabrication of long length tape was very much limited. By introducing $BaZrO_3$ barrier, for instance the AC loss was reduced from 0.9 to 0.37 mW/Am, while the critical current density decreased by 50%. Their difficulty seems to be originated from the brittleness of barrier materials. Further in order to increase the volume fraction of superconducting component in the tape and to increase the transparence of oxygen diffusion to superconducting Bi2223 core, the reduction of barrier thickness is highly requested.

In order to realize the requirements, we have tried to use metallic materials as a barrier. In the present study, the usefulness of metallic magnesium has been demonstrated by fabricating the silver sheathed multifilamentary Bi2223 tape including magnesium layer. During deformation, the Mg layer was very much thinned up to sub-micron thickness. By the successive oxidation treatment, the barrier was confirmed to become MgO layer.

II. Experimental Procedure

Firstly the monofilamentary wire with hexagonal shape was prepared as follows. Bi2223-oxide precursor was filled in the silver tube with dimension of 6.0/4.5 mm dia. Then the Mg tube with dimension of 7.0/6.0 mm dia was covered on the former Ag/Bi2223 composite. The whole composite was reduced in diameter up to 4.5 mm outer dia. at elevated temperature in air. Further the silver tube with dimension of 6.0/4.5 mm dia. was covered on the deformed composite. Again the new composite was reduced in diameter and finished by hexagonal shaped die with dimension of 1.0 mm by means of drawing at elevated temperature. At this step, the thickness of Mg layer was estimated to be 54 μm in average.

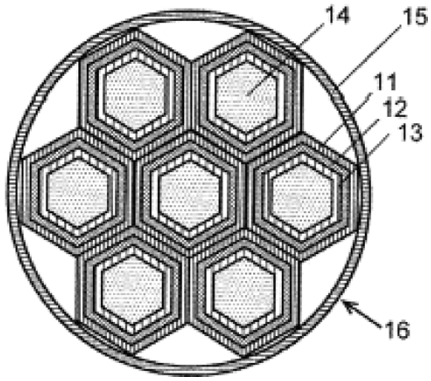

Fig. 1. Design of Mg-barriered multifilamentary Bi2223 composite. Here Ag(11 and 13), Mg(12), Bi2223(14), and Ag alloy(15). In the present study, the composite including 14 filaments has been actually fabricated.

In the second step, the multifilamentary wire is prepared as its design is indicated in Fig. 1 and the process is listed in Fig. 2. The composite with 14 filaments was grove-rolled and drawn at elevated temperature. Finally the wire was deformed to thin tape by means of rolling and pressing. The finally designed thickness of Mg layer was estimated to be 1.4 μm in average. During the plastic deformations at elevated temperature, we investigated optimum condition with changing temperatures between 523 and 723 K as the details are described later.

It is necessary to oxidize the Mg layer to MgO because a stable barrier can be provided. When the diffusion coefficient of oxygen in silver has been known, it is possible to predict the oxidation condition of temperature and time. From the limitation of phase stability of Ag-Mg system, the oxidization treatment was carried out at temperatures between 623 and 773 K.

In order to produce a sound microstructure of Bi2223 layer with high critical current density, the process of deformation and heat treatment was applied. The preliminary heat treatment was applied at the higher temperature than that for oxidation of magnesium. After the tape was rolled at room temperature by thickness reduction of 20 to 60%, it was heat treated under Ar-7.8% O_2 mixed gas.

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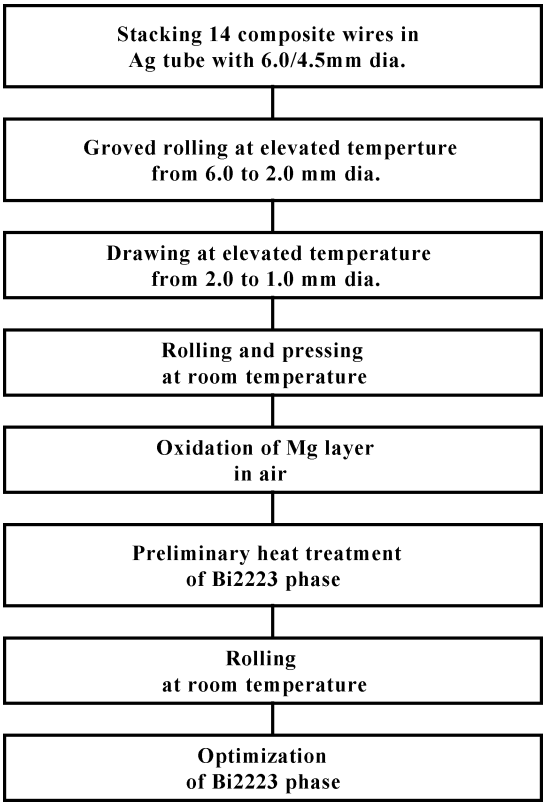

Fig. 2. Process manufacturing the multifilamentary Bi2223 tape with MgO barrier. Firstly the Bi2223 precursor powder was put in the single tube consisting of silver/magnesium/silver layer. Then 14 tubes filled by the powder were stacked as shown in Fig. 1.

In the present study, our efforts have been concentrated to establish the microstructure control for the Ag sheathed Bi2223 tape with ultra-thin MgO barrier. The phase change during deformation at elevated temperature and during oxidation were precisely investigated by means of XRD and SEM-EPMA.

III. Experimental Results and Discussion

A. Deformation at Elevated Temperature

In order to deform smoothly the composite, it was necessary to deform the composite at elevated temperatures, because the magnesium component is heavily work-hardened at room temperature. When the multifilamentary wire was drawn at temperatures above 523 K, the deformation resistance became weak and any fracture of wire was not observed during deformation.

The intermetallic compounds, however formed at the interface between Ag matrix and Mg layer as shown in Fig. 3. As recognized from the binary phase diagram of Ag and Mg system, $AgMg_3$ and AgMg have been identified. The higher temperature was applied for deformation, the thicker compound layers were produced. After long time annealing, a thin layer of Ag_3Mg phase was discernibly observed at the interface between AgMg compound and Ag matrix.

In order to investigate the time dependence of compound layer growth, wire samples were annealed at fixed temperature for various times. The change of thickness of each compound layer is shown as a function of square root of time in Fig. 4. The time evolution of layer growth is clear to obey the square

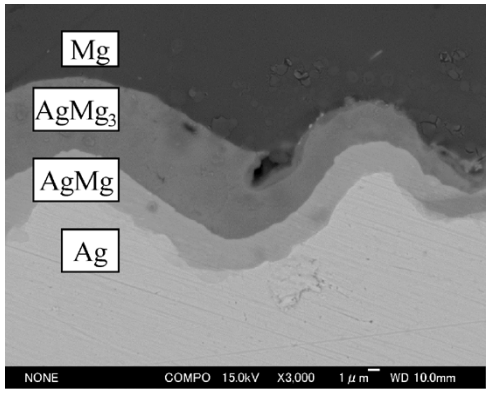

Fig. 3. Microphotograph of the area close to the interface between Ag matrix and Mg layer when the composite wire was annealed at 673 K under vacuum.

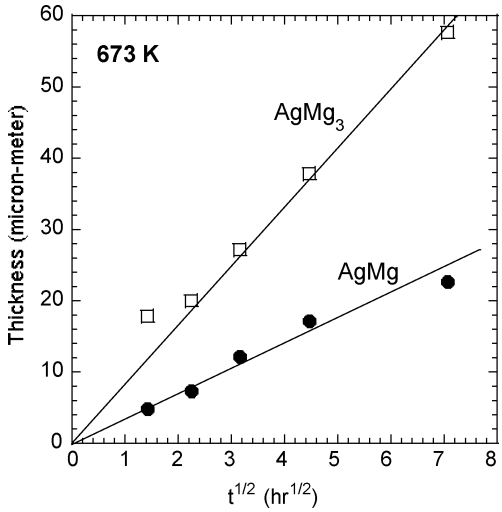

Fig. 4. Observed change of layer thickness as a function of square root of time when the sample was annealed at 673 K under vacuum.

root time dependence, which indicates the diffusion control for growth mechanism. Then the thickness change is given by the equations;

$$d_{AgMg3} = d^o_{AgMg3} t^{\frac{1}{2}} \exp\left(-\frac{Q_{AgMg3}}{RT}\right) \quad (1)$$

$$d_{AgMg} = d^o_{AgMg} t^{\frac{1}{2}} \exp\left(-\frac{Q_{AgMg}}{RT}\right) \quad (2)$$

where d^o_i, Q_i, and R are the proportional constant, activation energy and gas constant, respectively.

We examined the thickness change at three different temperatures of 623, 673, and 723 K, respectively. From the relation between the logarithm of thickness and the inverse temperature at the constant annealing time, the activation energy was determined to be 62.3 and 92.7 kJ/mol for $AgMg_3$ and AgMg compound, respectively, while proportional constant was 5.14×10^5 and 5.9×10^7 $\mu m/s^{1/2}$ for $AgMg_3$ and AgMg compound, respectively.

Now it is possible to judge how two types of intermetallic compound layer form at a given annealing condition. As shown in Fig. 5, the times to get 1 μm thick layer of $AgMg_3$ and AgMg compound layers are given as a function of annealing

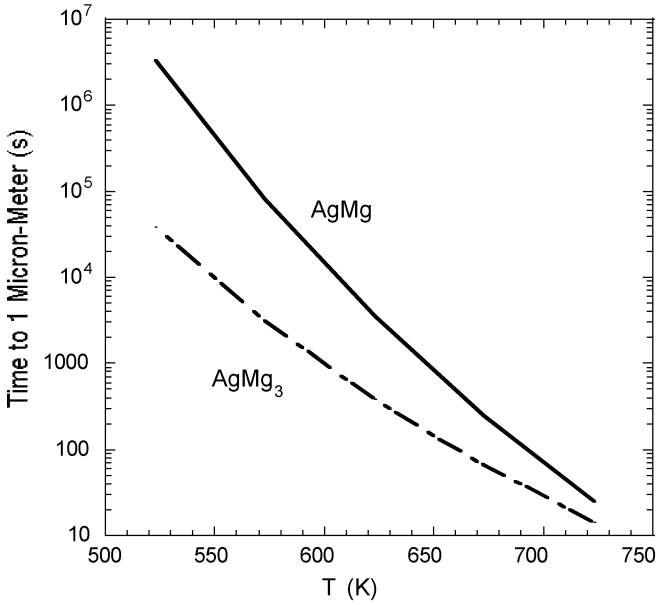

Fig. 5. Estimated time as a function of annealing temperature, when the layer thickness of AgMg and AgMg3 compound phases grows to one μm.

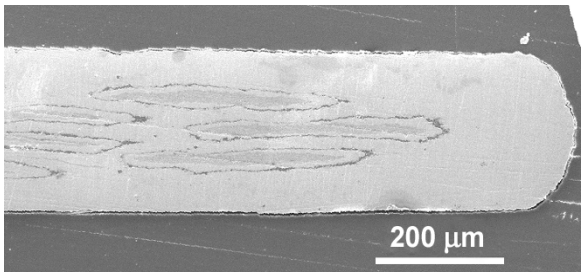

Fig. 6. Cross section of the tape including 14 Bi2223 cores. Each core is embedded in Ag matrix and surrounded by Mg barrier.

temperature. At temperatures below 573 K, where the deformation is used to be carried out, two compound layers are not produced when the deformation is finished within one hour. As mentioned later, however, two compounds are quickly produced within 100 second, when the oxidization treatment of Mg layer is carried out.

B. Oxidation of Magnesium Layer

According to the procedure indicated in Fig. 2, the tapes have been fabricated by a combination of rolling and pressing at room temperature. Fig. 6 shows a cross section of the tape just after deformation, of which tape thickness was 0.21 mm. The designed thickness of Mg layer was 1.4 μm in this deformation condition. Here the total time oxidizing Mg layer has been estimated, when the tape with 0.2 mm thick is placed under 1 atm oxygen atmosphere at temperature T (K), where the Mg layer with 2 μm thick locates at the center of tape as shown in Fig. 7. Here we assumed that the rate limiting process of oxidation is the oxygen diffusion in silver matrix. Then the total time is given by the equation;

$$t = \frac{x_{Mg} y_{Ag}}{n_O N_{av} D_{OinAg} (c_S - c_{Mg})} \tag{3}$$

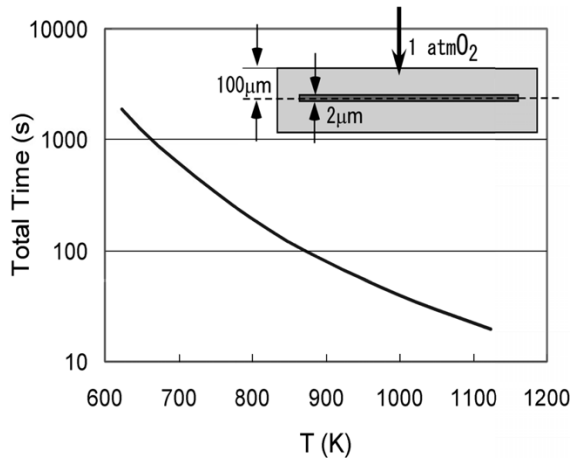

Fig. 7. Calculated total time for oxidizing Mg layer as a function of temperature, where 2 μm Mg layer is embedded in the 200 μm Ag matrix.

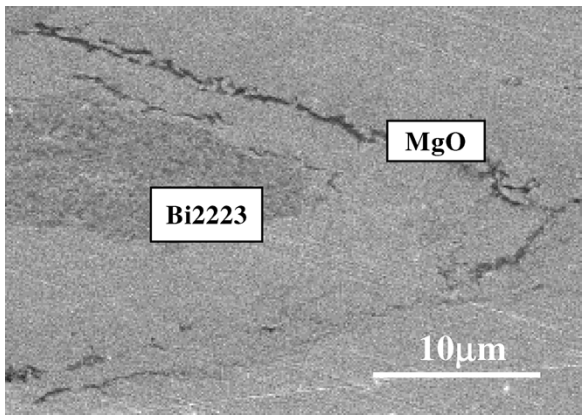

Fig. 8. Ultra-thin MgO layer located around the Bi2223 oxide core, when the sample was heat treated at 753 K. The MgO layer reached less than one μm.

where x_{Mg} is the thickness of Mg layer ($= 2$ μm), y_{Ag} is the thickness of Ag matrix ($= 100$ μm), n_O, N_{av}, D_{OinAg} are the number of oxygen per unit volume of MgO, Avogadro's number, and diffusion coefficient of oxygen in silver, respectively. c_S, c_{Mg} are the oxygen concentration at the surface to oxygen atmosphere and that at the interface to magnesium layer. The oxygen concentration at surface was determined from the solubility limit of oxygen in Ag at each temperature [4] and the oxygen concentration at the interface was assumed to be zero. The calculated result is indicated in Fig. 7. For instance, the total time is estimated to be 1.9 ks and 70 s when the oxidation is carried out at 623 K and 923 K, respectively. The present calculation suggests that the oxidation time of Mg layer depends greatly on temperature.

As mentioned in the Section III-A, Mg reacts with silver to form two types of compound at least. Further Mg tends to diffuse in the matrix when the sample keeps for long time at the higher temperature. Once Mg is oxidized, on the other hand, the oxidized layer is stabilized to remain there. Depending on temperature, however, the morphology of MgO phase changes from a tightly layered form to finely dispersed particles. So it is very important to choose the temperature for oxidation of Mg layer. Fig. 8 shows a stable ultra-thin MgO layer when the sample was heat treated at 753 K. In the present study, however

it was not possible to measure experimentally the growth rate of MgO layer because the precursory AgMg layer was very thin and oxidized easily after heating.

At the final stage, the tape with oxidized Mg layer was preliminary heat treated at 1095 K for 180 ks and then cold-rolled by different degree of reduction. The tape was heat treated at 1103 K for 144 ks under Ar-7.8%O_2 atmosphere and then gradually cooled down to 1060 K before air-quenching to room temperature. When the tape was cold-rolled by the degree more than 20%, the XRD peak of Bi2223 phase was observed and the superconductivity was confirmed by the transport critical current measurement.

Thus the present study has made clear the condition to form ultra-thin MgO barrier surrounding SC oxide cores. Further the whole condition to optimize both AC loss characteristics and engineering critical current has to be explored.

IV. Conclusion

An unique manufacturing process in order to reduce AC loss of high Tc superconducting tapes has been investigated. Firstly the Bi-oxide precursor is filled in the clad tube with Ag/Mg/Ag three layers. It is reduced in diameter and cut into short wires. Then they are bundled into the silver alloy tube and further reduced in diameter. Then it is rolled/pressed to get thin tapes. During the above process, the specimens are deformed at elevated temperatures. Each SC oxide core is surrounded by continuous metallic Mg layer with thickness less than 1 μm. The tape is heat treated at temperatures between 673 and 1073 K under oxygen atmosphere. Then Mg layers are oxidized. Tightly layered MgO phase was observed depending on the heat treatment conditions. After that, the tape with MgO barrier is heat treated at higher temperatures between 1053 and 1113 K under the reduced oxygen atmosphere to get fully superconducting Bi2223 phase. Their thin MgO barrier was confirmed to be stable and not to react at all with the SC layer. Thus the multifilamentary Bi2223 tape with very thin and continuous MgO barrier was successfully manufactured.

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